

SMR/1310 - 4

**SPRING COLLEGE ON
NUMERICAL METHODS IN ELECTRONIC STRUCTURE THEORY**

(7 - 25 May 2001)

**"Density functional theory, Kohn-Sham equations,
exchange-correlation functionals"**

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The Total Energy satisfies a variational principle directly in terms of the KS orbitals in presence of orthogonality constraints

$$E[\{\varphi_i\}] = \sum_i \langle \varphi_i | -\frac{\hbar^2}{2m} \nabla^2 | \varphi_i \rangle + \frac{e^2}{2} \int \frac{\rho(r) \rho(r')}{|r-r'|} d^3r d^3r' + E_{xc}[\rho] \\ + \int V_{\text{ext}}(r) \rho(r) d^3r + E_{\text{kin-ion}} - \sum_{i,j} \lambda_{ij} (\langle \varphi_i | \varphi_j \rangle - \delta_{ij})$$

with as usual $\rho(r) = \sum_i |\varphi_i(r)|^2$

The minimum condition for this functional reads:

$$0 = \frac{\delta E}{\delta \varphi_i^*(r)} = -\frac{\hbar^2}{2m} \nabla^2 \varphi_i(r) + \left[V_{\text{ext}}(r) + e^2 \int \frac{\rho(r')}{|r-r'|} d^3r' + \frac{\delta E_{xc}}{\delta \rho(r)} \right] \varphi_i(r) - \sum_j \lambda_{ij} \varphi_j(r) \\ = [h^{KS} \varphi_i(r) - \sum_j \lambda_{ij} \varphi_j(r)]$$

it is equivalent to the KS eqs. up to a unitary transformation in the occupied manifold (that does not change $\rho(r)$!)

⇒ Global minimization strategies

- steepest descent

$$\varphi_i^{\text{NEW}}(r) = \varphi_i^{\text{OLD}}(r) + \Delta t \cdot \left(-\frac{\delta E}{\delta \varphi_i^*(r)} \right) + \text{orthogonality}$$

- conjugate gradients

- Car-Parrinello dynamics

NB: φ 's at the minimum may not coincide with KS orbitals → \mathcal{U}

GC (or GGA) vs LDA

improves binding energies (better atomic energies)

(but Be_2 : $e_{\text{exp}} = 0.11 \text{ eV}$ LDA = 0.53 eV GC = 0.36 eV)

bond lengths of IIA and IIB homonuclear dimers are much better

water clusters and ice: much better geometries and energies

Si, Ge, GaAs are better in LDA (not the binding energy)

4d-5d metals: it is not clear

no improvement for the gap problem (nor for dielectric constants)

————— . —————
The improvement is not systematic and probably due to the wrong reason.

GGA are fitted on atomic total xc energies: locally they are not better than LDA

They do not satisfy known asymptotic behaviour

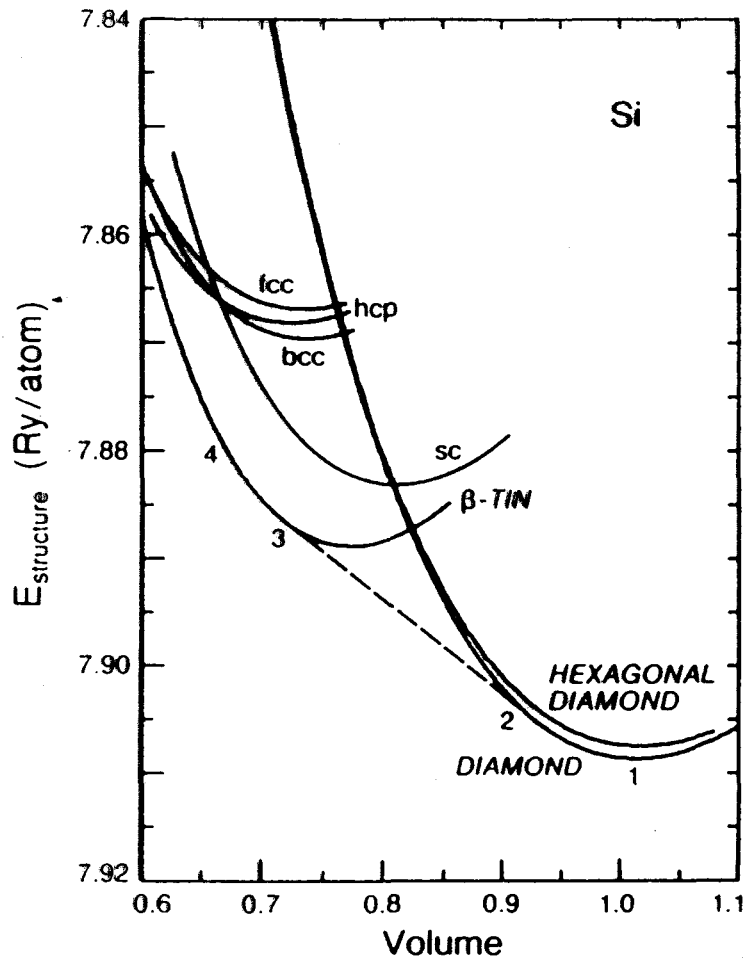
In an atom:

$V_{xc} \underset{r \rightarrow \infty}{\sim} -\frac{e^2}{r}$ while $V_{xc}^{\text{LDA, GGA}}$ vanishes exponentially

$V_{xc} \underset{r \rightarrow 0}{\Rightarrow} \text{const}$ while $V_{xc}^{\text{LDA}} \underset{r \rightarrow 0}{=} \text{const}$

$V_{xc}^{\text{GGA}} \underset{r \rightarrow 0}{=} -\infty$

Equation of State of Silicon



W.E. Pickett / Pseudopotential methods in condensed matter applications

Rev. M.T. Yin and M.L. Cohen Phys. Rev. B 26 5668 (1982)

U. Moll, M. Bockstedte, M. Fuchs, E. Pehlke and M. Scheffler

Phys. Rev. B 52 2550 (1995)

	LDA	GC	Exp
P_F (kbar)	80	122-146	103-125

Crystalline Selenium

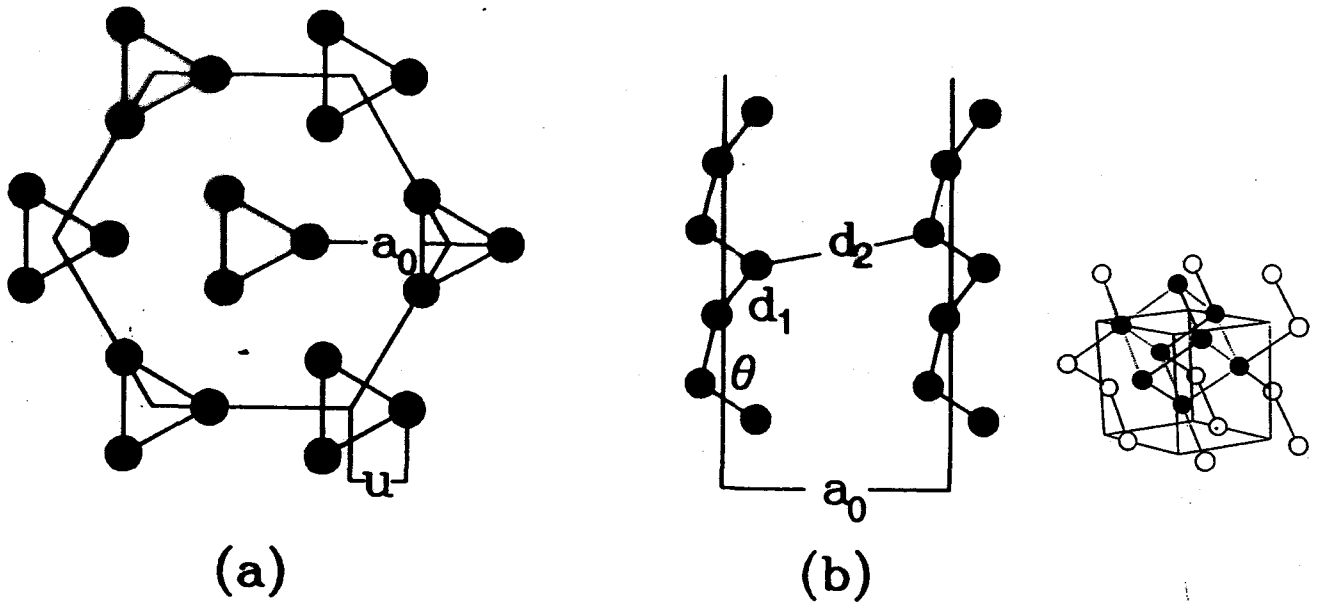


FIG. 1. Structure of selenium. (a) Projection on the basal plane of the selenium helices. a_0 is the length of the hexagonal edge, while u is the radius of the helices. (b) Side view of the chains: d_1 is the covalent (intrachain) bond length, while d_2 is the interchain bond length.

Lengths in a.u.

	d_1	d_2	θ	a_0	c	u	ua_0
LDA	4.61	5.84	103°	7.45	9.68	0.256	1.91
GC	4.57	6.60	105°	8.29	9.78	0.224	1.86
Expt.	4.51	6.45	102.7°	8.23	9.37	0.228	1.88

A. Dal Corso and R. Resta Phys. Rev. B 50 4327 (1994)

- Water, Ice..

Compute XC potential: GGA case

$$E_{xc}^{GGA}[P] = \int F_{xc}^{GGA}(P(r), \sigma(r) = |\nabla P(r)|) P(r) d^3r$$

by definition:

$$\delta E_{xc}^{GGA}[P] = \int \frac{\delta E_{xc}^{GGA}[P]}{\delta P(r)} \cdot \delta P(r) d^3r$$

Making the density variation in the above formula

$$\delta E_{xc}^{GGA}[P] = \int \left\{ \frac{\partial}{\partial P} \left(F_{xc}^{GGA}(P, \sigma) P \right) \Big|_{\substack{P=P(r) \\ \sigma=\sigma(r)}} \delta P(r) + \frac{\partial}{\partial \sigma} \left(F_{xc}^{GGA}(P, \sigma) P \right) \Big|_{\substack{P=P(r) \\ \sigma=\sigma(r)}} \delta \sigma(r) \right\} d^3r$$

integrating the second term by part

$$\delta E_{xc}^{GGA}[P] = \int \left\{ \frac{\partial}{\partial P} \left(F_{xc}^{GGA}(P, \sigma) P \right) \Big|_{\substack{P=P(r) \\ \sigma=\sigma(r)}} - \sum_{\mu=1}^3 \frac{\partial}{\partial \sigma} \left[\frac{\partial}{\partial \sigma} \left(F_{xc}^{GGA}(P, \sigma) P \right) \Big|_{\substack{P=P(r) \\ \sigma=\sigma(r)}} \cdot \frac{\partial_{\mu} P(r)}{\sigma(r)} \right] \right\} \delta P(r) d^3r$$

hence

$$v_{xc}^{GGA}(r) = \frac{\partial}{\partial P} \left(F_{xc}^{GGA}(P, \sigma) P \right) \Big|_{\substack{P=P(r) \\ \sigma=\sigma(r)}} - \sum_{\mu=1}^3 \frac{\partial}{\partial \sigma} \left[\frac{\partial}{\partial \sigma} \left(F_{xc}^{GGA}(P, \sigma) P \right) \Big|_{\substack{P=P(r) \\ \sigma=\sigma(r)}} \cdot \frac{\partial_{\mu} P(r)}{\sigma(r)} \right]$$

\downarrow
 LDA-like

GGA correction only

TABLE IV. Known properties of the exact density functional

Property	E_{xc}^{LDA} Ref. [4]	E_{xc}^{LM} Ref. [34]	E_{xc}^{PW91} Ref. [36]	E_x^{B88} Ref. [37]	E_x^{ECMV} Ref. [34]	E_c^{WL} Ref. [39]	E_c^{LYP} Ref. [40]
1 $\rho_x(\mathbf{r}, \mathbf{r}') \leq 0$	(Y)	-	(Y)	-	-	-	-
2 $\int \rho_x(\mathbf{r}, \mathbf{r}') d\mathbf{r}' = -1$	(Y)	-	(Y)	-	-	-	-
3 $\int \rho_c(\mathbf{r}, \mathbf{r}') d\mathbf{r}' = 0$	(Y)	-	(Y)	-	-	-	-
4 $E_x[\rho] < 0$	(Y)	(Y)	(Y)	(Y)	(Y)	-	-
5 $E_c[\rho] \leq 0$	(Y)	(N)	(N)	-	-	(N)	(N)
6 $E_x[\rho], E_{xc}[\rho] \geq -c \int \rho^{4/3} dr$ ^a	(Y)	(N)	(Y)	(Y)	(N)	-	-
7 $E_x[\rho_\lambda] = \lambda E_x[\rho]$ ^b	(Y)	(Y)	(Y)	(Y)	(Y)	-	-
8 $E_c[\rho_\lambda] < \lambda E_c[\rho], \lambda < 1$ ^c	(Y)	(N)	(Y)	-	-	(N)	(N)
9 $\lim_{\lambda \rightarrow \infty} E_c[\rho_\lambda] > -\infty$	(N)	(Y ^J)	(Y ^J)	-	-	(Y)	(Y)
10 $\lim_{\lambda \rightarrow 0} \frac{1}{\lambda} E_c[\rho_\lambda] > -\infty$	(Y)	(N)	(Y)	-	-	(Y)	(Y)
11 $\lim_{\lambda \rightarrow \infty} E_x[\rho_\lambda^x] > -\infty$ ^c	(N)	(N)	(Y)	(N)	(N)	-	-
12 $\lim_{\lambda \rightarrow 0} E_x[\rho_\lambda^x] > -\infty$	(Y)	(N)	(Y)	(Y)	(Y)	-	-
13 $\lim_{\lambda \rightarrow \infty} \frac{1}{\lambda} E_x[\rho_\lambda^{xy}] > -\infty$ ^d	(Y)	(N)	(Y)	(Y)	(Y)	-	-
14 $\lim_{\lambda \rightarrow 0} \frac{1}{\lambda} E_x[\rho_\lambda^{xy}] > -\infty$	(N)	(N)	(Y)	(N)	(N)	-	-
15 $\lim_{\lambda \rightarrow \infty} \lambda E_c[\rho_\lambda^x] > -\infty$	(N)	(Y ^J)	(Y)	-	-	(N)	(N)
16 $\lim_{\lambda \rightarrow 0} \frac{1}{\lambda} E_c[\rho_\lambda^x] = 0$	(N)	(N)	(Y)	-	-	(N)	(N)
17 $\lim_{\lambda \rightarrow \infty} E_c[\rho_\lambda^{xy}] = 0$	(N)	(N)	(Y)	-	-	(N)	(N)
18 $\lim_{\lambda \rightarrow 0} \frac{1}{\lambda^2} E_c[\rho_\lambda^{xy}] > -\infty$	(N)	(Y ^J)	(Y)	-	-	(N)	(N)
19 $\epsilon_x(r) \rightarrow -\frac{1}{2r}, r \rightarrow \infty$	(N)	(N)	(N)	YN ^g	(N)	-	-
20 $v_x(r) \rightarrow -\frac{1}{r}, r \rightarrow \infty$	(N)	(N)	(N)	(N)	(N)	-	-
21 $v_x(r), v_c(r) \rightarrow \text{finite value}, r \rightarrow 0$	(Y)	(N)	(N)	(N)	(N)	(N)	(N)
22 LDA limit for constant $\rho(\mathbf{r})$	(Y)	(N)	(Y)	(Y)	(Y)	(N)	(N)

^a $1.44 < c < 1.68$

^b $\rho_\lambda(\mathbf{r}) = \lambda^3 \rho(\lambda \mathbf{r})$; ^c $\rho_\lambda^x(\mathbf{r}) = \lambda \rho(\lambda x, y, z)$; ^d $\rho_\lambda^{xy}(\mathbf{r}) = \lambda^2 \rho(\lambda x, \lambda y, z)$

^e Note that $E_c[\rho_\lambda] < \lambda E_c[\rho], \lambda < 1$ is equivalent to $E_c[\rho_\lambda] > \lambda E_c[\rho], \lambda > 1$.

^f But it diverges to $+\infty$

^g "Y" for exponential $\rho(\mathbf{r})$, but "N" in general, e.g. $\epsilon_x^{B88}(r) \rightarrow -1/r$ for a gaussian.

$$E_{xc}[\rho] = \int e_{xc}(\rho, \nabla\rho, \nabla^2\rho) d^3r$$

$$k_F = (3\pi^2\rho)^{1/3}, \quad k_s = \left(\frac{4}{\pi}k_F\right)^{1/2}, \quad s = \frac{|\nabla\rho|}{2k_F\rho},$$

$$t = \frac{|\nabla\rho|}{2k_s\rho}, \quad r_s = \left(\frac{3}{4\pi\rho}\right)^{1/3}.$$

All the parameters that appear in the following functionals are in atomic units.

LDA exchange functional:

$$e_x^{\text{LDA}} = A_x \rho^{4/3}, \tag{A2}$$

where $A_x = -(3/4)(3/\pi)^{1/3}$.

LDA correlation functional (Perdew-Wang¹³):

$$e_c^{\text{LDA}} = -2a\rho(1 + \alpha_1 r_s) \times \log \left[1 + \frac{1}{2a(\beta_1 r_s^{1/2} + \beta_2 r_s + \beta_3 r_s^{3/2} + \beta_4 r_s^2)} \right], \tag{A3}$$

where $a = 0.0310907$, $\alpha_1 = 0.21370$, $\beta_1 = 7.9957$, $\beta_2 = 3.5876$, $\beta_3 = 1.6382$, and $\beta_4 = 0.49294$.

Langreth-Mehl exchange-correlation functional:¹⁰

$$e_x = e_x^{\text{LDA}} - a \frac{|\nabla\rho|^2}{\rho^{4/3}} \left(\frac{7}{9} + 18f^2 \right), \tag{A4}$$

$$e_c = e_c^{\text{RPA}}(\rho) + a \frac{|\nabla\rho|^2}{\rho^{4/3}} (2e^{-F} + 18f^2), \tag{A5}$$

where $F = b|\nabla\rho|/\rho^{7/6}$, $b = (9\pi)^{1/6}f$, $a = \pi/(16(3\pi^2)^{4/3})$, and $f = 0.15$.

Perdew-Wang '86 exchange functional:¹⁴

$$e_x = e_x^{\text{LDA}}(\rho) \left(1 + 0.0864 \frac{s^2}{m} + b s^4 + c s^6 \right)^m, \tag{A6}$$

where $m = 1/15$, $b = 14$ and $c = 0.2$.

Perdew-Wang '86 correlation functional:¹⁵

$$e_c = e_c^{\text{LDA}}(\rho) + e^{-\Phi} C_c(\rho) \frac{|\nabla\rho|^2}{\rho^{4/3}}, \tag{A7}$$

where

$$\Phi = 1.745 \tilde{f} \frac{C_c(\infty)}{C_c(\rho)} \frac{|\nabla\rho|}{\rho^{7/6}},$$

$$C_c(\rho) = C_1 + \frac{C_2 + C_3 r_s + C_4 r_s^2}{1 + C_5 r_s + C_6 r_s^2 + C_7 r_s^3}, \tag{A8}$$

and $\tilde{f} = 0.11$, $C_1 = 0.001667$, $C_2 = 0.002568$, $C_3 = 0.023266$, $C_4 = 7.389 \times 10^{-6}$, $C_5 = 8.723$, $C_6 = 0.472$, $C_7 = 7.389 \times 10^{-2}$.

Perdew-Wang '91 exchange functional:¹¹

$$e_x = e_x^{\text{LDA}}(\rho) \left[\frac{1 + a_1 s \sinh^{-1}(a_2 s) + (a_3 + a_4 e^{-100s^2}) s^2}{1 + a_1 s \sinh^{-1}(a_2 s) + a_5 s^4} \right], \tag{A9}$$

where $a_1 = 0.19645$, $a_2 = 7.7956$, $a_3 = 0.2743$, $a_4 = -0.1508$, and $a_5 = 0.004$.

Perdew-Wang '91 correlation functional:¹¹

$$e_c = [e_c^{\text{LDA}}(\rho) + \rho H(\rho, s, t)], \tag{A10}$$

where

$$H = \frac{\beta^2}{2\alpha} \log \left[1 + \frac{2\alpha}{\beta} \frac{t^2 + A t^4}{1 + A t^2 + A^2 t^4} \right] + C_{c0} [C_c(\rho) - C_{c1}] t^2 e^{-100s^2},$$

$$A = \frac{2\alpha}{\beta} [e^{-2\alpha\epsilon_c(\rho)/\beta^2} - 1]^{-1},$$

and $\alpha = 0.09$, $\beta = 0.0667263212$, $C_{c0} = 15.7559$, $C_{c1} = 0.003521$. The function $C_c(\rho)$ is the same as for the Perdew-Wang '86 correlation functional. $\epsilon_c(\rho)$ is defined so that $e_c^{\text{LDA}}(\rho) = \rho\epsilon_c(\rho)$.

Becke '88 exchange functional:⁸

$$e_x = e_x^{\text{LDA}}(\rho) \left[1 - \frac{\beta}{2^{1/3} A_x} \frac{x^2}{1 + 6\beta x \sinh^{-1}(x)} \right], \tag{A11}$$

where $x = 2(6\pi^2)^{1/3} s = 2^{1/3} |\nabla\rho|/\rho^{4/3}$, $A_x = (3/4)(3/\pi)^{1/3}$, and $\beta = 0.0042$.

Wilson-Levy correlation functional:¹²

$$e_c = \frac{a\rho + b|\nabla\rho|/\rho^{1/3}}{c + d|\nabla\rho|/(\rho/2)^{4/3} + r_s}, \tag{A12}$$

where $a = -0.74860$, $b = 0.06001$, $c = 3.60073$, and $d = 0.90000$.

Closed shell Lee-Yang-Parr correlation functional:¹⁶

$$e_c = -a \frac{1}{1 + d\rho^{-1/3}} \left[\rho + b\rho^{-2/3} \left[C_F \rho^{5/3} - 2t_W + \frac{1}{9} \times \left(t_W + \frac{1}{2} \nabla^2 \rho \right) \right] e^{-c\rho^{-1/3}} \right], \tag{A13}$$

where

$$t_W = \frac{1}{8} \left(\frac{|\nabla\rho|^2}{\rho} - \nabla^2 \rho \right), \tag{A14}$$

and $C_F = 3/10(3\pi^2)^{2/3}$, $a = 0.04918$, $b = 0.132$, $c = 0.2533$, and $d = 0.349$.

Perdew-Burke-Ernzerhof PRL 77 3865(9c)

¹P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).
²W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1976).
³N. R. Kestner and O. Sinanoglu, Phys. Rev. 128, 2687 (1962).
⁴P. M. Laufer and J. B. Krieger, Phys. Rev. A 33, 1480 (1986).
⁵S. Kais et al., J. Chem. Phys. 99, 417 (1993).
⁶M. Taut, Phys. Rev. A (in press).
⁷C. Umrigar and X. Gonze (unpublished).
⁸A. D. Becke, Phys. Rev. A 33, 3098 (1988).

Generalized Gradient Approximations (GGA)

Local Density Approximation

$$E_{xc}^{LDA}[n] = \int n(r) \epsilon_{xc}^{hom}(n(r)) d^3r$$

to go beyond LDA make a gradient expansion

$$E_{xc}^{GC}[n] = \int \left[n(r) \epsilon_{xc}(n(r)) + C(n(r)) \frac{|\nabla n|^2}{n^{4/3}} + \dots \right] d^3r$$

- improves LDA for slowly varying density $\frac{|\nabla n|}{n} \ll 1$
- gives worse results for realistic systems
- sum-rules for $n_{xc}(r, r')$ are not fulfilled

GGA

$$E_{xc}^{GGA}[n] = \int n(r) \epsilon_{xc}(n(r)) d^3r + \int \epsilon_{xc}[n(r), |\nabla n(r)|] d^3r$$

the correction function, ϵ_{xc} , is chosen to satisfy formal conditions for the xc hole and fit to exact xc energies for atoms

NOT A UNIQUE RECIPE

- tendency to favour more homogeneous systems
- Overbinding of molecules and solids
-
- Good chemical trends

in good systems (covalent, metallic, ionic bonds
bonding from region of high density)

- geometry is good
- bondlengths and angles within a few %
- phonons within a few %
- dielectric, piezoelectric constant ~10% too large

in bad systems: weakly bonded systems (H-bonded
Van der Waals)

much too short bondlengths, large overbinding

Atoms: $-\frac{e^2}{r}$, dissociation limit

-strongly correlated systems

IB and IIB Dimers

	R_e [a.u.]		D_e [eV]		ω_e [cm^{-1}]		
	Exp	LSD	Exp	LSD	Exp	LSD	
	Cu_2	4.20	4.07	1.97	3.18	265	295
IB	Ag_2	4.67	4.69	1.66	2.67	192	207
	Au_2	4.67	4.63	2.30	3.25	191	193
	Zn_2	7.56	5.29*	0.06	0.23	—	78
IIB	Cd_2	9.10	5.77*	0.05	0.24	—	67
	Hg_2	6.86	5.65*	0.07	0.23	—	71

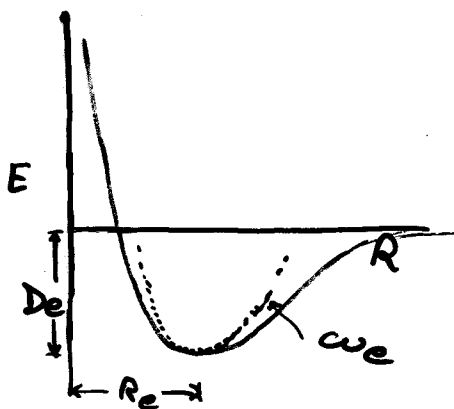
LSD: P. Ballone and G. Galli, Phys. Rev. B 42 1112 (1990)

Cr_2	3.17	3.17	1.56	2.6	470	441
		3.2	1.44	2.8		470

LSD: Boykers et al. Mol. Phys. 52 291 (1984)

Bernholc and Holzwarth Phys Rev. Lett. 50 1451 (1983)

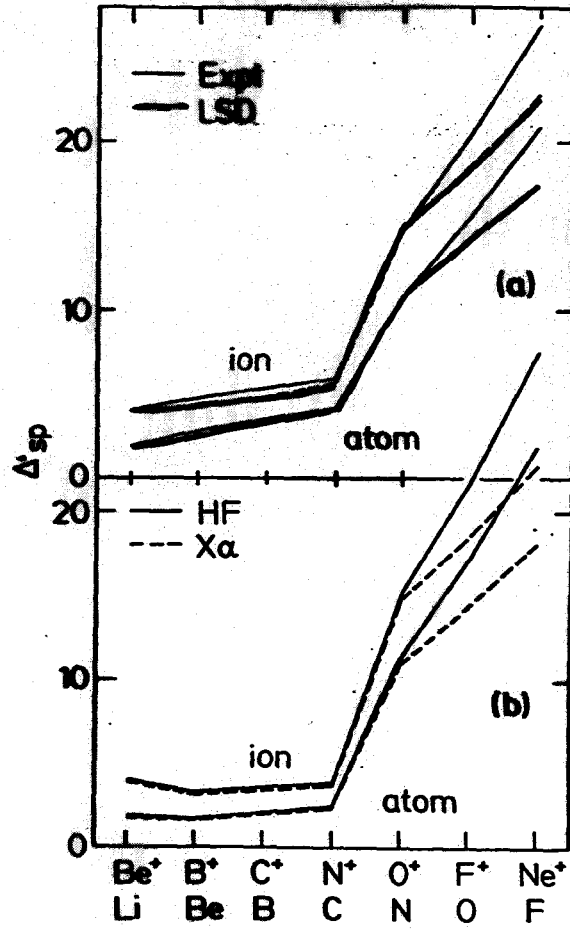
First-Row Dimers



	R_e [a.u.]		D_e [eV]		ω_e [cm^{-1}]		
	Exp	LSD	Exp	LSD	Exp	LSD	
H_2	1.40	1.45	4.75	4.91	4400	4277	
Li_2	5.05	5.12	1.06	1.01	351	347	
Be_2	4.71	4.63	0.11	$0.50^* 0.4$	294	362^*	23%
B_2	3.04	3.03	3.08	3.93	1051	1082	
C_2	2.35	2.36	6.31	7.19	1857	1869	
N_2	2.07	2.08	9.91	11.34	2358	2387	
O_2	2.28	2.31	5.23	$7.54^* 2.2$	1580	1610	
F_2	2.68	2.62	1.66	$3.32^* 1.7$	892	1069^*	19%

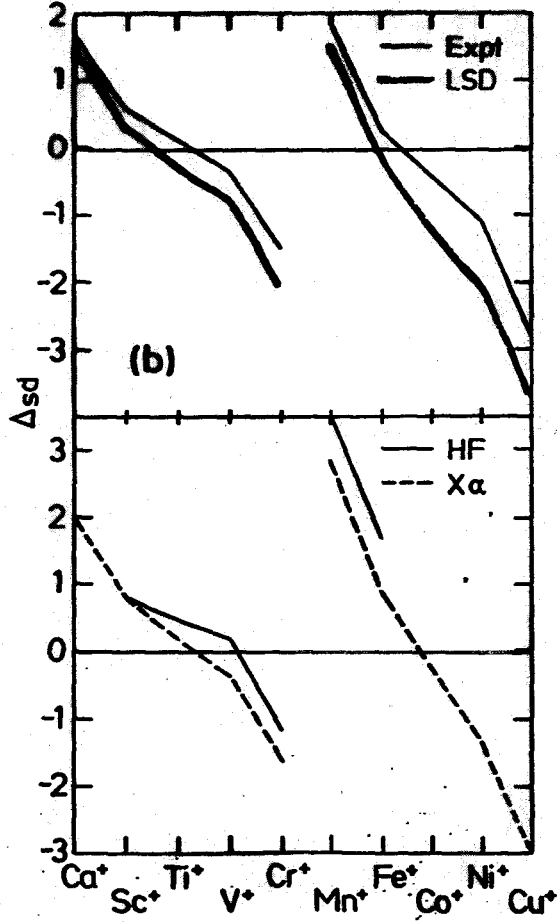
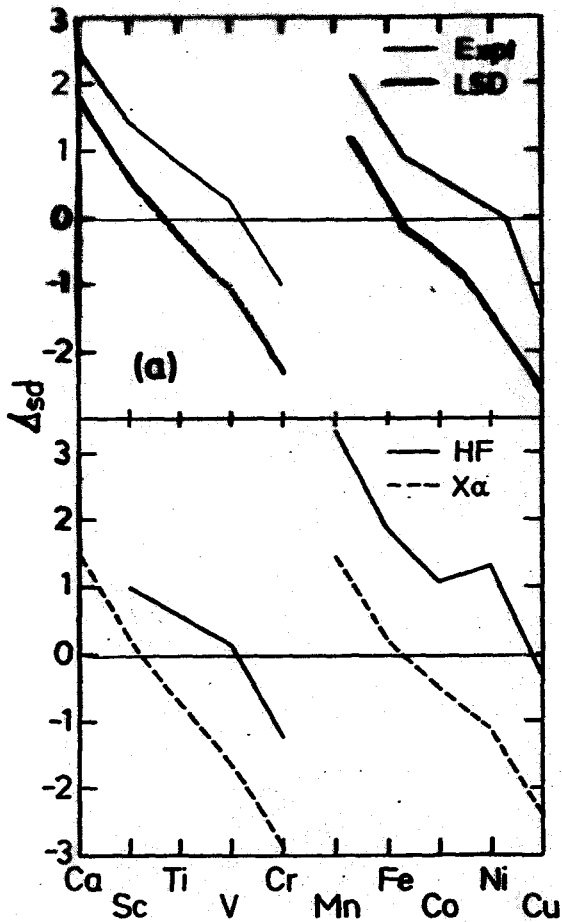
LSD G.S. Painter and F.W. Averill Phys. Rev. B 26 1781 (1982)

TRANSFER ENERGIES IN ATOMS



$$\Delta_{sp} = E(1s^2 2s 2p^{n-1}) - E(1s^2 2s^2 2p^{n-2})$$

$$\Delta_{sd} = E([core] 3d^{n-1} 4s^1) - E([core] 3d^{n-2} 4s^2)$$



R.O. Jones and O. Gunnarsson
 Rev. Mod. Phys., Vol. 61, No. 3, July 1989

ATOMIC IONIZATION ENERGIES

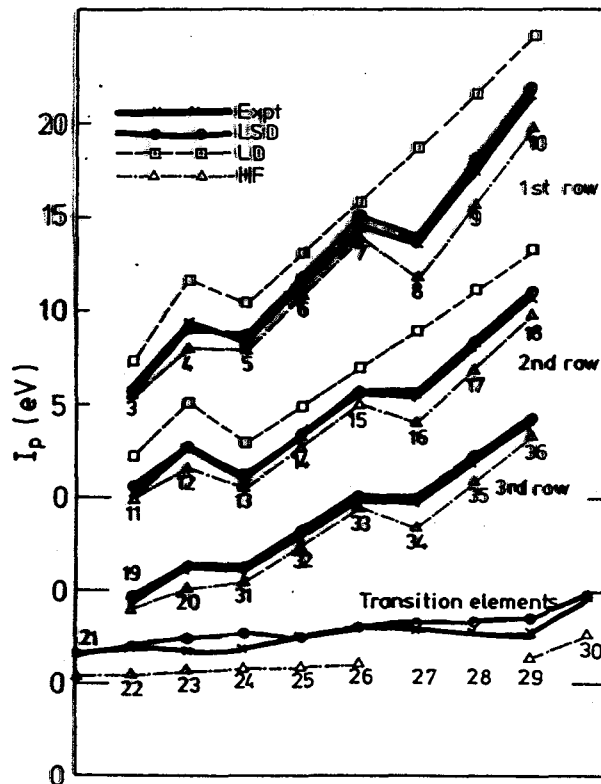


FIG. 8. First ionization energy of atoms in the local-density (LD), local spin-density (LSD), and Hartree-Fock (HF) approximations compared with experiment. The numbers show the atomic numbers of the atoms considered. For reasons of clarity, the zero of energy is shifted by 5, 10, and 15 eV for the second row, the third row, and the transition-element row, respectively. The LD results for the first and second rows are increased by an additional 2 eV.

R.O. Jones and O. Gunnarsson
 Rev. Mod. Phys., Vol. 61, No. 3, July 1989

	I^{exp}	$I^{LSD-\Delta SCF}$	I^{LSD-N}	[eV]
Li	5.4	5.7	3.4	
Be	9.3	9.1	5.7	
B	8.3	8.8	4.2	
C	11.3	12.1	6.3	
N	14.5	15.3	6.5	
O	13.6	14.2	7.4	
F	17.4	18.4	10.5	
Ne	21.6	22.6	13.3	
				↳ LSDA (non DFT) problem.

TOTAL ENERGIES OF FIRST-ROW ATOMS

	E^{exp}	E^{HF}	E^{LSD}	[Ry]
				$1H=2Ry$
Li	-14.957	-14.866	-14.686	
Be	-29.339	-29.150	-28.892	
B	-49.318	-49.070	-48.704	
C	-75.715	-75.404	-74.932	
N	-109.228	-108.856	-108.256	
O	-150.225	-149.716	-149.042	
F	-199.618	-198.982	-198.216	

E^{exp} C.W. Scherr, J.N. Silverman, F.A. Matsen, Phys. Rev. 127, 830 (1962)

E^{HF} E. Clementi, C. Roetti, At. Data Nucl. Data Tables 14 177 (1974)

E^{LSD} M.R. Norman, D.D. Koelling, Phys. Rev. B 30 5530 (1984)

SPIN-DENSITY FUNCTIONAL THEORY

introduce the possibility of coupling to a magnetic field

$$n(\mathbf{r}) \rightarrow n_{\alpha}(\mathbf{r}) \rightarrow (n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r}))$$

$$E[n_{\uparrow}, n_{\downarrow}] = T_S[n_{\uparrow}, n_{\downarrow}] + E_H[n] + E_{xc}[n_{\uparrow}, n_{\downarrow}] + \int V_{\text{ext}}^{(\alpha)} n(\mathbf{r}) d^3r + \int B(\mathbf{r}) m(\mathbf{r}) d^3r$$

$$T_S = \sum_{\alpha} \sum_i |\nabla \varphi_i^{\alpha}(\mathbf{r})|^2 \quad \alpha = \uparrow, \downarrow$$

$$E_{xc}^{\text{LSDA}} = \int n(\mathbf{r}) \epsilon_{xc}^{\text{hom}}(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})) d^3r$$

$$\text{KS. eqs.} \left\{ \begin{array}{l} \left[-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{KS}}^{\alpha}(\mathbf{r}) \right] \varphi_i^{\alpha}(\mathbf{r}) = \epsilon_i^{\alpha} \varphi_i^{\alpha}(\mathbf{r}) \\ n_{\alpha}(\mathbf{r}) = \sum_i |\varphi_i^{\alpha}(\mathbf{r})|^2 \\ V_{\text{KS}}^{\alpha}(\mathbf{r}) = V_{\text{ext}}^{(\alpha)} \pm B(\mathbf{r}) + V_H(\mathbf{r}) + \frac{\delta E_{xc}}{\delta n_{\alpha}} \end{array} \right. \quad n(\mathbf{r}) = \sum_{\alpha} n_{\alpha}(\mathbf{r}), \quad m(\mathbf{r}) = n_{\uparrow}(\mathbf{r}) - n_{\downarrow}(\mathbf{r})$$

electrons have spin degrees of freedom and are correlated differently according to it but within DFT V_{xc} is spin independent...

$$\psi(r, \sigma) = f(r) \cdot \chi(\sigma) \quad \chi = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Degenerate GS \rightarrow $n(r)$ is a statistical average
 $m(r) = n_{\uparrow}(r) - n_{\downarrow}(r) = 0$

this is correct BUT is difficult to implement in simple approximations for Exc

LDA is unsatisfactory in a number of cases

Slightly inhomogeneous electron gas

$$n(\mathbf{r}) = n_0 + \delta n(\mathbf{r}) = n_0 + \sum_{\mathbf{q}} \delta n_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}}$$

$$F[n] = F[n_0] + \frac{1}{2} \int \delta n(\mathbf{r}) \chi^{-1}(\mathbf{r}, \mathbf{r}') \delta n(\mathbf{r}') = F[n_0] + \frac{1}{2} \sum_{\mathbf{q}} \chi^{-1}(\mathbf{q}) |\delta n_{\mathbf{q}}|^2$$

$$\chi^{-1}(\mathbf{q}) = \chi_0^{-1}(\mathbf{q}) - v_c(\mathbf{q}) - f_{xc}(\mathbf{q})$$

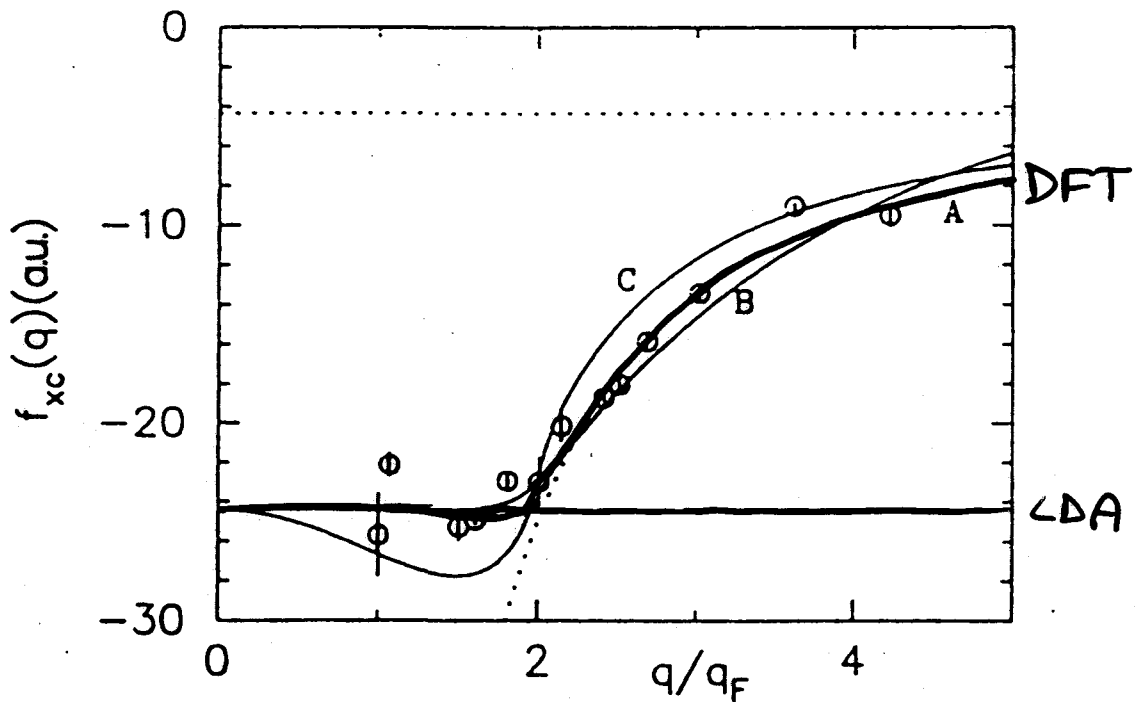


FIG. 2. Exchange-correlation factor $f_{xc}(q)$ of the electron gas at $r_s = 5$. The circles give the present MC results, with the curve A being an interpolation of the calculated points [see Eq. (7)] and curves B and C showing two approximations [14,15]. The horizontal dashed and dotted lines give, respectively, $f_{xc}(0)$ and $f_{xc}(\infty)$, while the dotted curve gives the large q behavior of $f_{xc}(q)$.

S. Moroni, D. Ceperley and G. Senatore Phys. Rev. Lett. **75** 689 (1995)

Exchange-Correlation Hole in Atoms

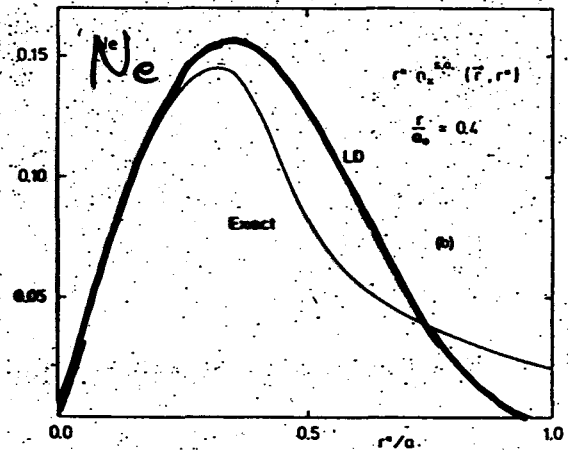
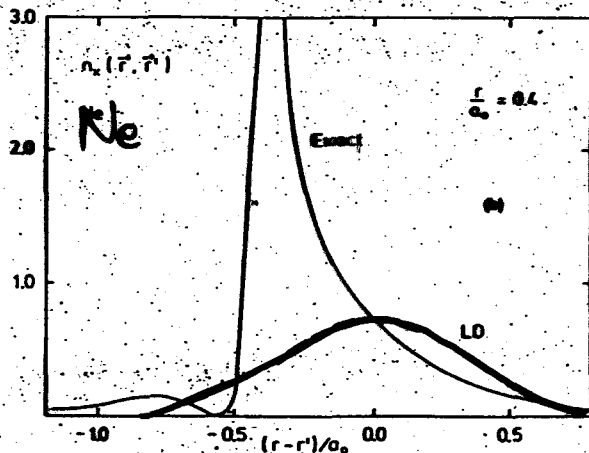
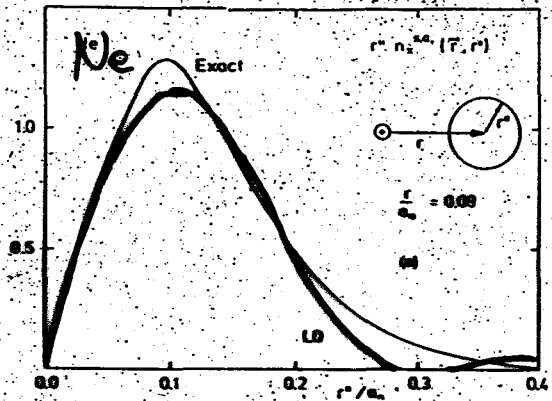
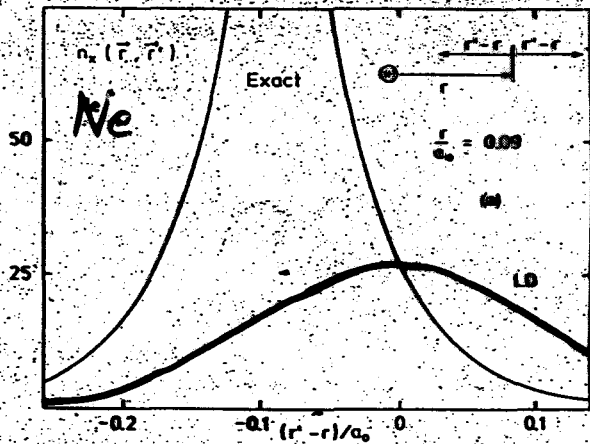


FIG. 5. Exchange hole $n_x(\vec{r}, \vec{r}')$ for a neon atom. The full curves show exact results and the dashed curves show the results in the LD approximation. The curves in (a) and (b) are for two different values of r .

FIG. 7. Spherical average of the neon exchange hole [Eq. (17)] times r'' for (a) $r=0.09$ a. u. and (b) $r=0.4$ a. u. The full curves give the exact results and the dashed curves are obtained in the LD approximation.

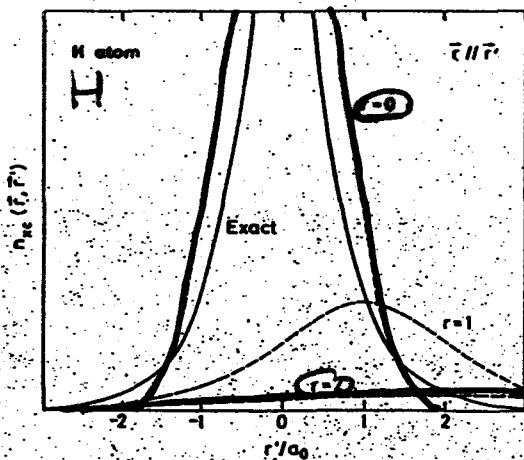


FIG. 4. Exchange-correlation hole $n_{xc}(\vec{r}, \vec{r}')$ (Eq. 15) for a hydrogen atom. The full curve shows the exact hole, while the dashed curves depict the hole in the LD approximation [Eq. (16)] for various positions of the electron (0, 1, and 2 a.u. from the proton), using the dielectric function of Singwi *et al* (Ref. 37). The x-axis gives the distance from the nucleus.

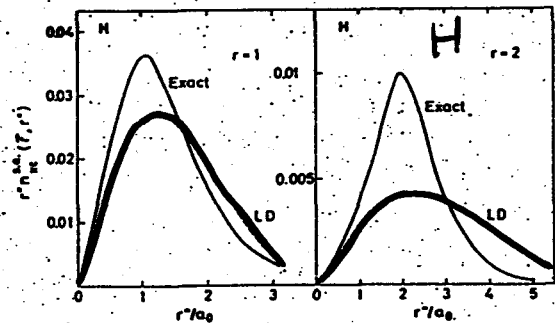


FIG. 6. Spherical average of the hydrogen XC hole [Eq. (16)] times r'' for $r=1$ and 2 a.u. as a function of r'' . The full curves give the exact results and the dashed curves are calculated in the LD approximation.

Ground State of the Electron Gas by a Stochastic Method

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(Received 16 April 1980)

An exact stochastic simulation of the Schrodinger equation for charged bosons and fermions has been used to calculate the correlation energies, to locate the transitions to their respective crystal phases at zero temperature within 10%, and to establish the stability at intermediate densities of a ferromagnetic fluid of electrons.

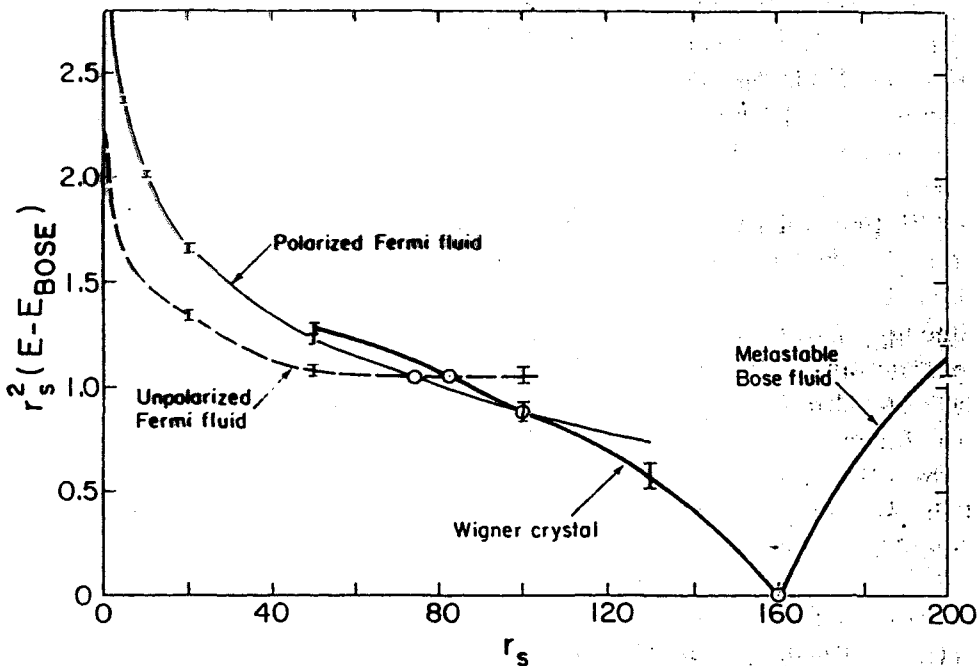


FIG. 2. The energy of the four phases studied relative to that of the lowest boson state times r_s^2 in rydbergs vs r_s in Bohr radii. Below $r_s = 160$ the Bose fluid is the most stable phase, while above, the Wigner crystal is most stable. The energies of the polarized and unpolarized Fermi fluid are seen to intersect at $r_s = 75$. The polarized (ferromagnetic) Fermi fluid is stable between $r_s = 75$ and $r_s = 100$, the Fermi-Wigner crystal above $r_s = 100$, and the normal paramagnetic Fermi fluid below $r_s = 75$.

LOCAL DENSITY APPROXIMATION (LDA)

since $g(r, r', \lambda) - 1$ is "short ranged"

$$n_{xc}(r, s) \cong n_{xc}^{hom}(r, s; n=n(r))$$

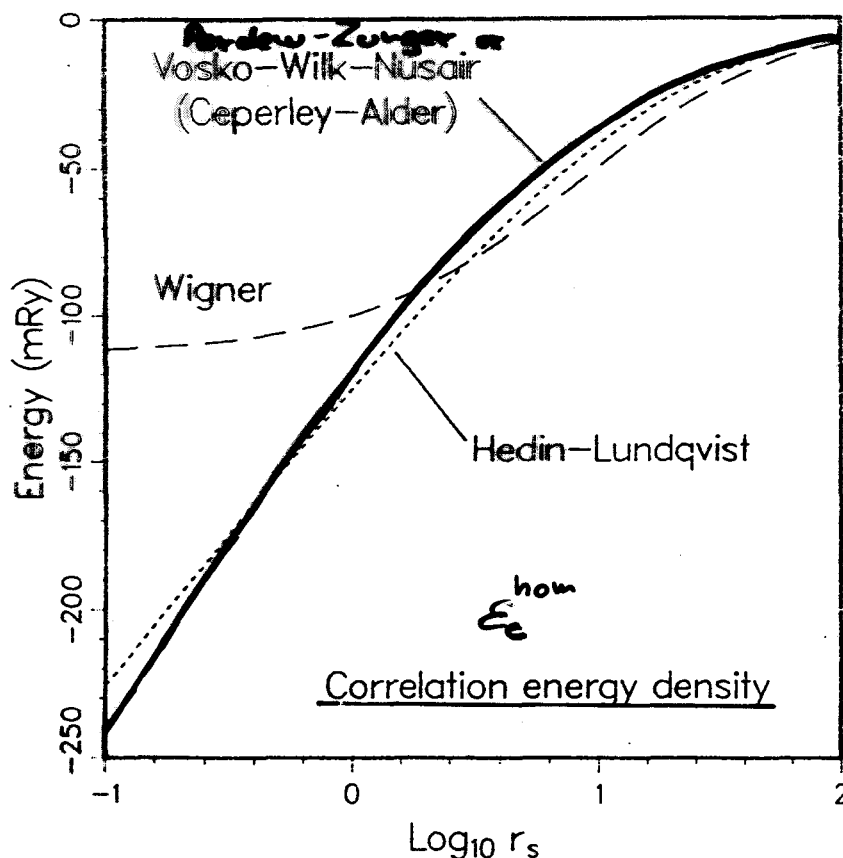
$$E_{xc}^{LDA} = \int d^3r n(r) E_{xc}^{hom}(n(r))$$

$$E_{xc}^{hom}(n) = E_x^{hom}(n) + E_c^{hom}(n)$$

$$E_x^{hom}(n) = -\frac{2}{9\pi} e^2 (3\pi^2 n)^{4/3}$$

$E_c^{hom}(n)$ from accurate DMC data

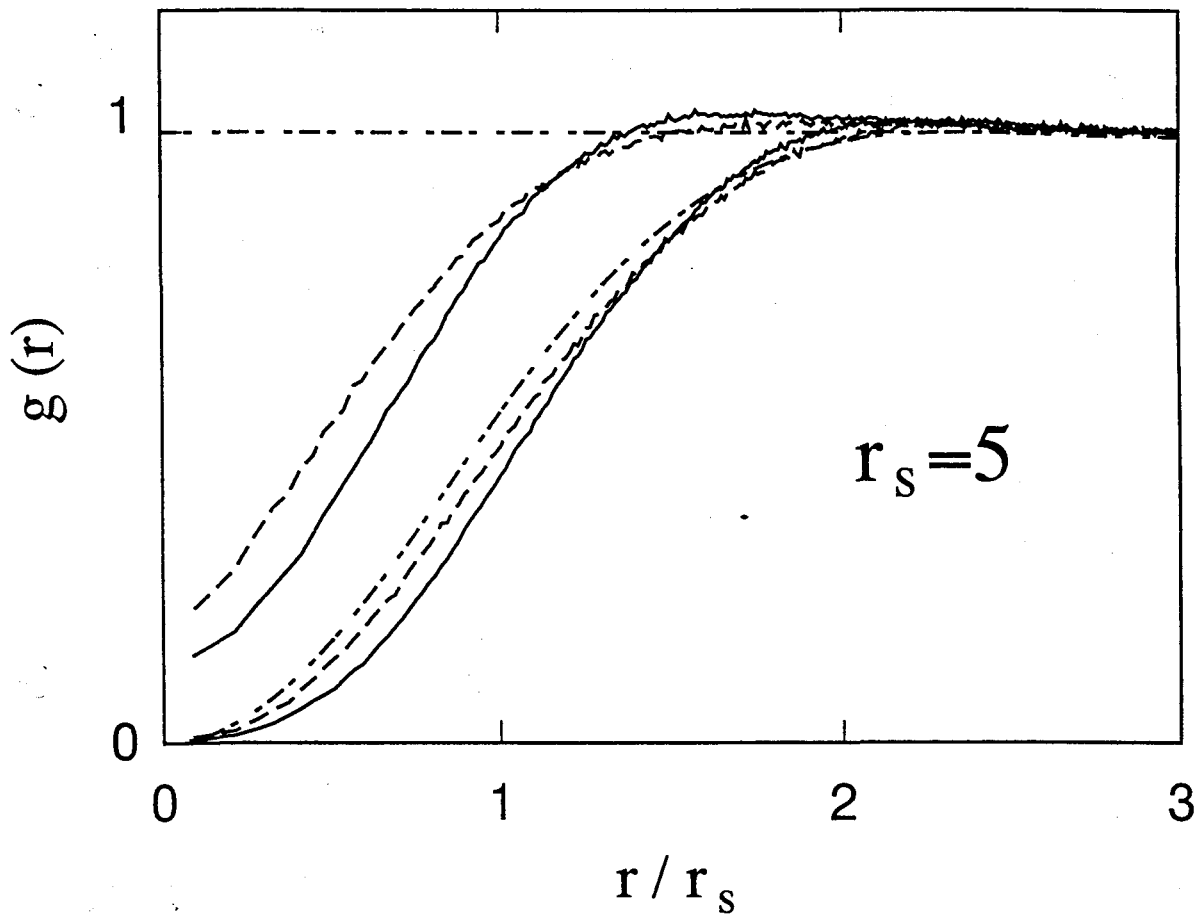
Ceperley - Alder
Phys. Rev. Lett 45, 566 ('80)



$$n = \frac{1}{\frac{4}{3}\pi r_s^3}$$

$$V_{xc}^{LDA}(r; [n]) = \frac{\delta}{\delta n(r)} E_{xc}^{LDA}[n] = \left. \frac{d(n \cdot E_{xc}^{hom}(n))}{dn} \right|_{n=n(r)}$$

ZERO PARAMETER THEORY!



$$F[n] = T_S[n] + \int_0^1 d\lambda \langle \psi_\lambda | U | \psi_\lambda \rangle$$

$$F[n] = T_S[n] + \int_0^1 d\lambda \int d^3r d^3r' \frac{e^2}{2} \frac{1}{|r-r'|} n(r) n(r') g(r, r', \lambda)$$

$g(r, r', \lambda)$ = pair correlation function with interaction λU

$g(r, r', \lambda) \rightarrow 1$ for $|r-r'| \rightarrow \infty \quad \forall \lambda$
 $(g(r, r', \lambda) - 1) \rightarrow 0$

$$F[n] = T_S[n] + \frac{e^2}{2} \int d^3r d^3r' \frac{n(r) n(r')}{|r-r'|} + \underbrace{\frac{e^2}{2} \int d^3r d^3r' \frac{n(r) n(r')}{|r-r'|} \int_0^1 d\lambda [g(r, r', \lambda) - 1]}_{E_{xc}}$$

$$n_{xc}(r, r'-r) = n(r') \int_0^1 d\lambda [g(r, r', \lambda) - 1] \quad \text{exchange-correlation hole}$$

$$\int n_{xc}(r, r'-r) d^3r' = -1$$

$$E_{xc} = \frac{e^2}{2} \int d^3r d^3r' \frac{n(r)}{|r-r'|} n_{xc}(r, r'-r) \\ = \frac{e^2}{2} \int d^3r n(r) \int d^3s \frac{1}{|s|} n_{xc}(r, s)$$

Formal expression for $E_{xc}[n]$
via coupling constant Integration

$$\hat{H}^{(\lambda)} = \hat{T}_e + \lambda U + V_{\text{ext}}^{(\lambda)}$$

$$F_{\lambda}[n] = \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \lambda U | \Psi \rangle = \langle \Psi_{\lambda} | \hat{T} + \lambda U | \Psi_{\lambda} \rangle$$

$V_{ee} = \frac{1}{2} \sum_{i,j} \frac{e^2}{|r_i - r_j|}$

non-interacting electrons: $\lambda = 0$

$$F_0[n] = T_S[n]$$

$$V_0 = V_{KS}$$

interacting electrons: $\lambda = 1$

$$F_1[n] = F[n]$$

$$V_1 = V_{\text{ext}}$$

$$F[n] = T_S[n] + \int_0^1 d\lambda \frac{dF_{\lambda}}{d\lambda}$$

$$F[n] = T_S[n] + \int_0^1 d\lambda \langle \Psi_{\lambda} | U | \Psi_{\lambda} \rangle$$

in HF theory there are the so called

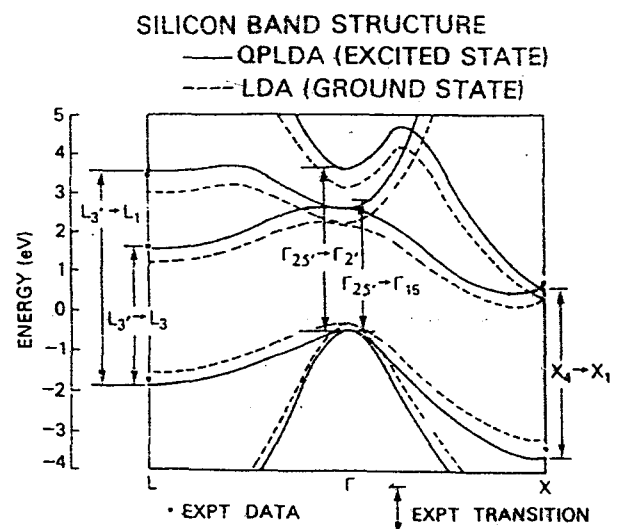
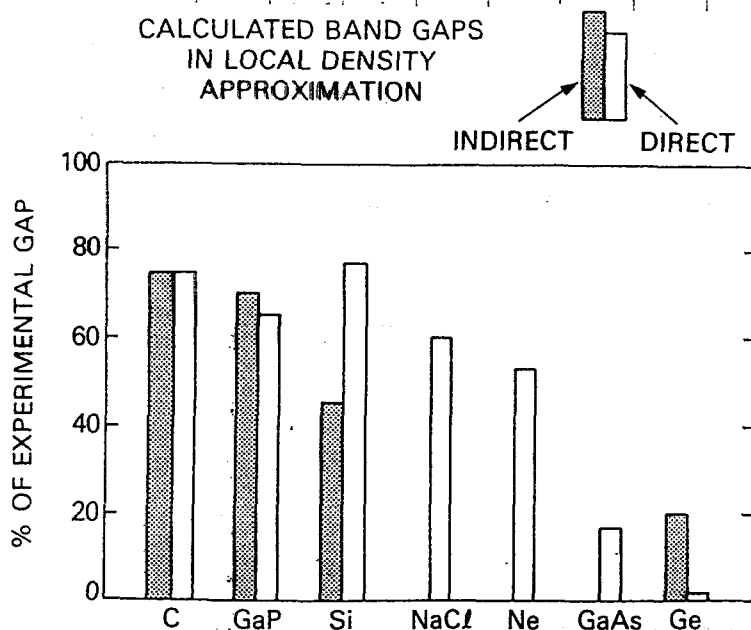
Koopman's Theorems

- I) $E_{\text{lost}}^{\text{HF}} \approx -I$ ionization energy
- II) $E_{\text{lost}+1}^{\text{HF}} \approx -A$ electron affinity
- III) $E_{\text{lost}+1}^{\text{HF}} - E_{\text{lost}}^{\text{HF}} \approx E_{\text{gap}}$

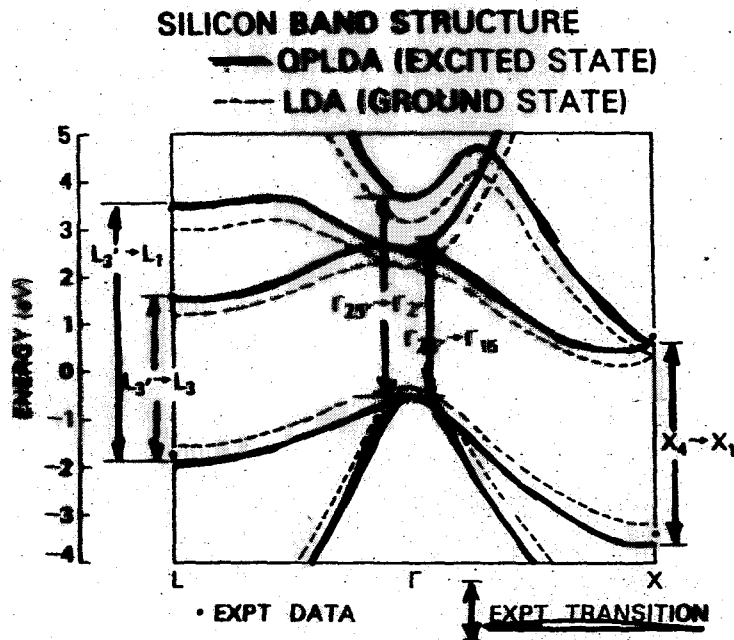
in DFT E_i 's have no physical meaning (they do not refer to the interacting system but to the fictitious KS's one) so there's no analogue of Koopman's theorems but for the first one which is exact

$$E_{\text{lost}}^{\text{DFT}} = -I$$

Band Gaps are substantially underestimated in semiconductors and insulators by DFT (or LDA?)

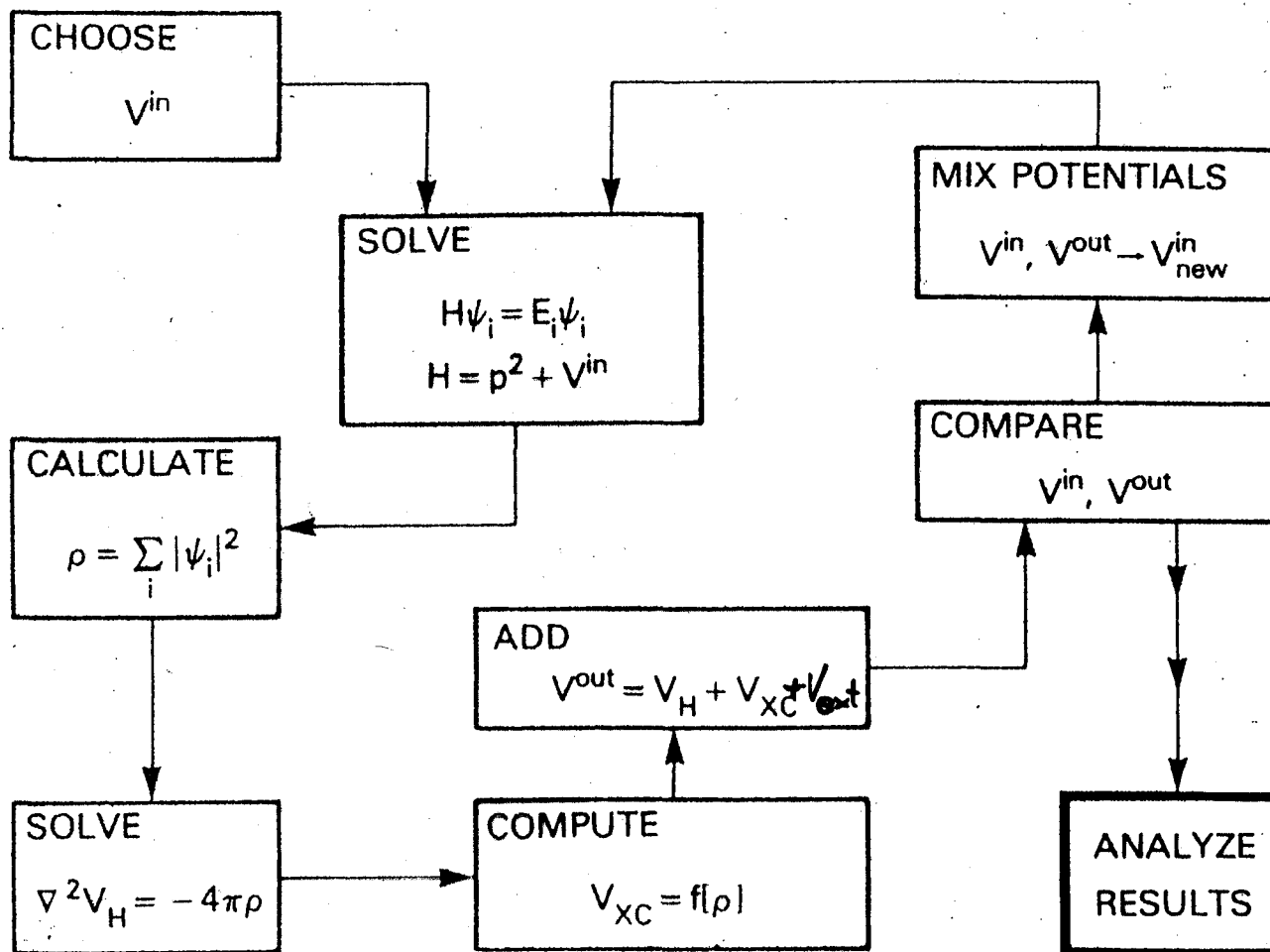


WARNING: K-S eigenvalues and wavefunctions are auxiliary quantities without direct physical meaning



- Band gaps are systematically underestimated by DFT
- The shape of the band structure is usually correct
- KS wavefunctions are good approx. of QP amplitudes
- More complex treatments (like GW) start from KS results
- Together with the charge density, band structure, DOS, wavefunctions give information on the nature of the system studied

SELF-CONSISTENCY IN DENSITY FUNCTIONAL THEORY



Total Energy

$$E = F[\rho] + \int V_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} + E_{\text{ion-ion}}$$

$$= T_0[\rho] + E_H[\rho] + E_{xc}[\rho] + \int V_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} + E_{\text{ion-ion}}$$

the minimum condition is:

$$0 = \frac{\delta E}{\delta \rho(\mathbf{r})} = \frac{\delta T_0[\rho]}{\delta \rho(\mathbf{r})} + V_H(\mathbf{r}) + v_{xc}(\mathbf{r}) + V_{\text{ext}}(\mathbf{r})$$

↓

$-V_{\text{KS}}(\mathbf{r})$ from the variational principle of the non-interacting auxiliary problem.

the Kohn-Sham eqs. are:

$$\begin{cases} \left[-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{KS}}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}) \\ \rho(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2 \\ V_{\text{KS}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r}) + v_{xc}(\mathbf{r}) \end{cases}$$

where

$$\begin{cases} V_H(\mathbf{r}) = e^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \\ v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})} \end{cases}$$

The KS eqs are a set of self-consistent equations

$$V_{\text{KS}}^{(\text{in})}(\mathbf{r}) \longrightarrow \phi_i(\mathbf{r}) \longrightarrow \rho(\mathbf{r}) \longrightarrow V_{\text{KS}}^{(\text{out})}(\mathbf{r})$$

at the minimum

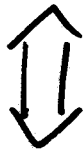
$$\boxed{V_{\text{KS}}^{(\text{in})}(\mathbf{r}) = V_{\text{KS}}^{(\text{out})}(\mathbf{r})}$$

Kohn - Sham eqs.

$$E[n] = T_S[n] + E_H[n] + E_{xc}[n] + \int V_{\text{ext}}(r) n(r) d^3r$$

$$\mu' = \frac{\delta E[n]}{\delta n(r)} = \frac{\delta T_S}{\delta n(r)} + V_H^{(r)} + \frac{\delta E_{xc}}{\delta n(r)} + V_{\text{ext}}^{(r)} \quad \text{interacting system}$$

$$\mu' = \frac{\delta E_S[n]}{\delta n(r)} = \frac{\delta T_S}{\delta n(r)} + V_{\text{KS}}^{(r)} \quad \text{non-interacting system}$$



$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{KS}}(r) \right] \varphi_i(r) = \epsilon_i \varphi_i(r)$$
$$n(r) = \sum_i |\varphi_i(r)|^2$$
$$V_{\text{KS}}(r) = V_{\text{ext}}(r) + V_H(r) + V_{xc}(r)$$

φ_i 's are auxiliary wfs

ϵ_i 's have no direct physical meaning

Kohn - Sham equations

the minimum condition for the interacting system is

$$\delta \left[F[n] + \int V_0(r) n(r) d^3r - \mu \left(\int n(r) d^3r - N \right) \right] = 0$$

$$\frac{\delta F[n]}{\delta n(r)} + V_0(r) - \mu = 0$$

$$\frac{\delta T_s[n]}{\delta n(r)} + e^2 \int \frac{n(r')}{|r-r'|} d^3r' + \frac{\delta E_{xc}^{[n]}}{\delta n(r)} + V_0(r) - \mu = 0$$

let V_{KS} be the potential of the non-interacting system that gives $n(r)$

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{KS}(r) \right] \phi_i(r) = \epsilon_i \phi_i(r)$$

$$\psi(r_1, \dots, r_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(r_1) & \dots & \phi_1(r_N) \\ \vdots & & \vdots \\ \phi_N(r_1) & \dots & \phi_N(r_N) \end{vmatrix}$$

$$n(r) = \sum_i |\phi_i(r)|^2$$

$$\delta \left[T_s[n] + \int V_{KS}(r) n(r) d^3r - \mu \left(\int n(r) d^3r - N \right) \right] = 0$$

$$\frac{\delta T_s}{\delta n(r)} + V_{KS}(r) - \mu = 0$$

$$V_{KS}(r) = V_0(r) + e^2 \int \frac{n(r')}{|r-r'|} d^3r' + \frac{\delta E_{xc}^{[n]}}{\delta n(r)}$$

It is useful to introduce a fictitious system of non-interacting electrons

$$\text{HK: } n(r) \rightarrow T_s[n] = \min_{\psi \rightarrow n} \langle \psi | \hat{T}_e | \psi \rangle$$

$$F[n] = T_s[n] + E_H[n] + E_{xc}[n]$$

↑
definition of E_{xc}

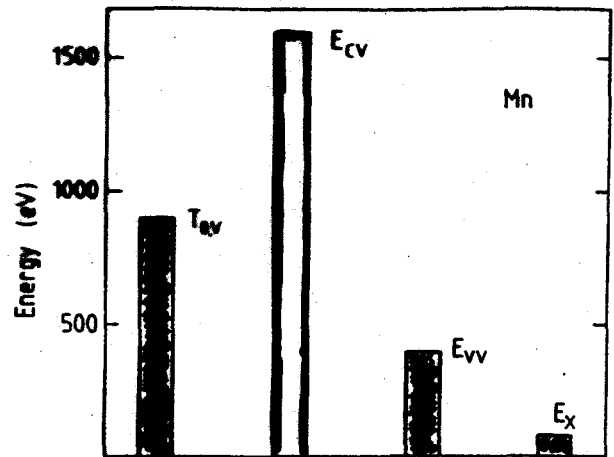


FIG. 4. Relative magnitudes of contributions to total valence energy of Mn atom (in eV).

$$E[n] = T_s[n] + E_H[n] + E_{xc}[n] + \int V_{ext}(r) n(r) d^3r$$

$F[n]$ is a very non-trivial functional of the density $n(r)$

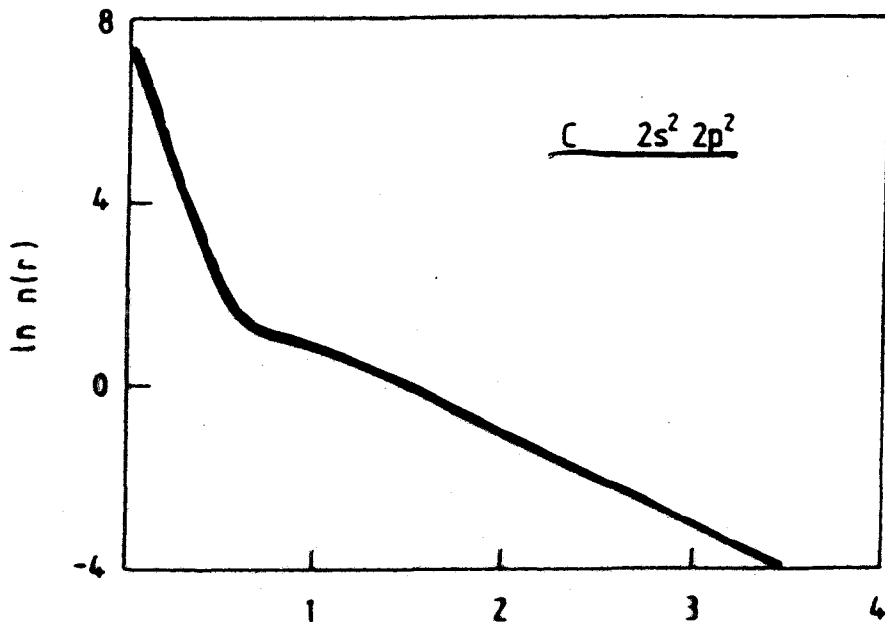


FIG. 1. Spherically averaged density $n(r)$ in ground state of carbon atom as a function of distance r from nucleus.

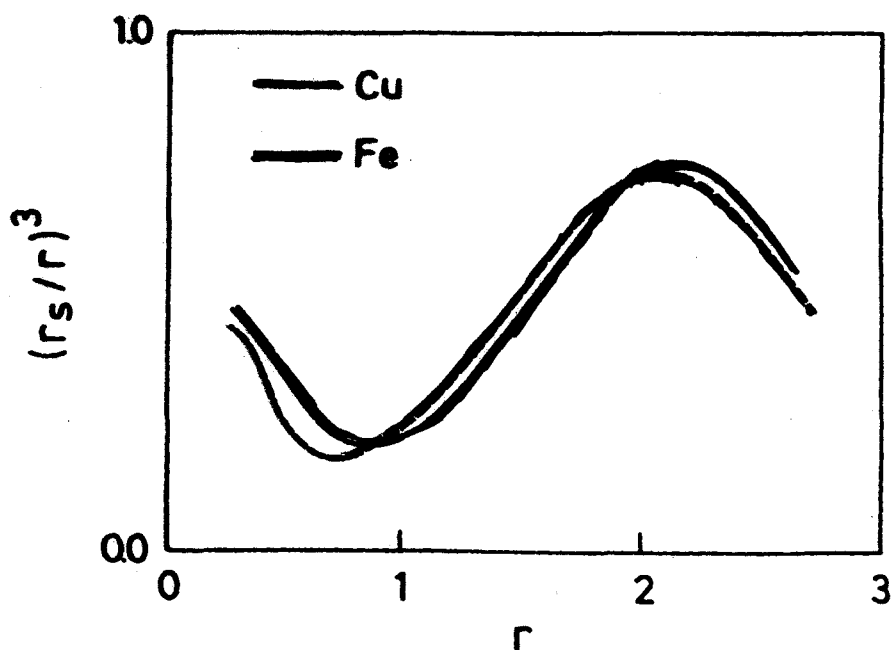
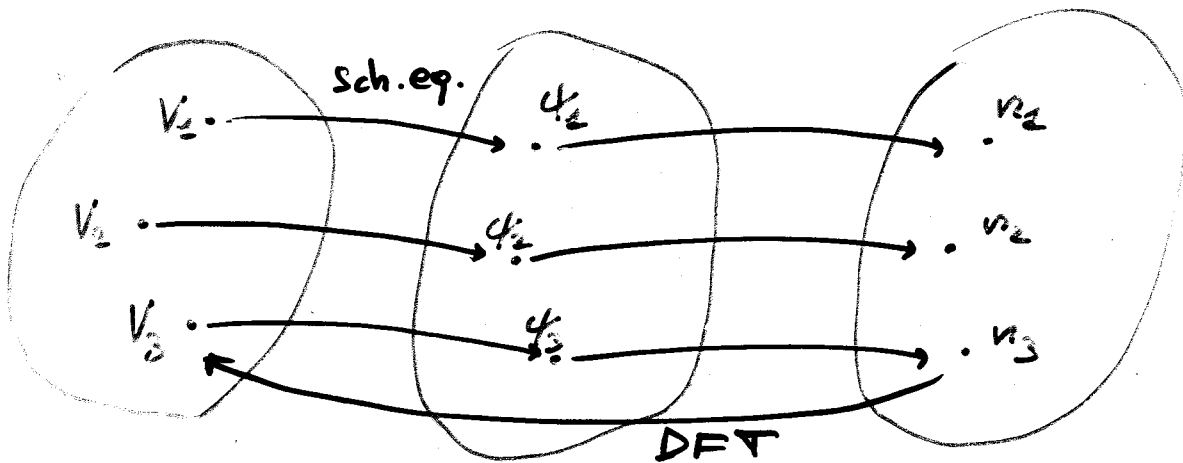


FIG. 6. Density of metallic Fe and Cu as a function of the radius r . The density n is expressed in terms of the parameter r_s , where $n = (4\pi r_s^3/3)^{-1}$.

DENSITY FUNCTIONAL THEORY

the density as the basic variable (for GS properties)

$$[T_e + V_{ee} + V] \psi_{GS} = E_{GS} \psi_{GS} ; \quad n(r) = \langle \psi_{GS} | \hat{n}(r) | \psi_{GS} \rangle$$



Hohenberg & Kohn Theorem Phy. Rev. 136 3864 (1964)

if $V'(r) \neq V(r) + \text{const}$ then $n'(r) \neq n(r)$

$$\Rightarrow n(r) \rightarrow V(r) + \text{const} \rightarrow \psi_{GS} \rightarrow E_{GS}, \dots$$

$$F[n] = \langle \psi_{GS}^{[n]} | T_e + V_{ee} | \psi_{GS}^{[n]} \rangle$$

$$E[n] = F[n] + \int V(r) n(r) d^3r$$

$F[n]$ is a well defined functional of $n(r)$

$E[n]$ is minimized by the true GS density

and $E[n_{GS}] = E_{GS}$

test charge: q



$$E_{q\text{-test}}(\mathbf{r}) = q \left[\sum_V \frac{Z_V e}{|\mathbf{R}_V - \mathbf{r}|} + \int \frac{-e n(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} \right]$$

$$q = -e$$



$$E(\mathbf{r}) = - \sum_V \frac{Z_V e^2}{|\mathbf{R}_V - \mathbf{r}|} + e^2 \int \frac{n(\mathbf{r}') + \delta n(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d^3 r'$$

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{ion}}(\mathbf{r}) + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d^3 r' + v_{\text{screen}}(\mathbf{r}) \right] \varphi_i(\mathbf{r}) = \epsilon_i \varphi_i(\mathbf{r})$$

electrons are Fermions

$$\Psi(r_1, \dots, r_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(r_1) & \dots & \varphi_1(r_N) \\ \vdots & & \vdots \\ \varphi_N(r_1) & \dots & \varphi_N(r_N) \end{vmatrix}$$

$$n(\mathbf{r}) = \sum_{i=1}^N |\varphi_i(\mathbf{r})|^2$$

Self Consistent Field

the screening term contains contributions due to the statistics (exchange) and static and dynamical correlations

Many properties are within the scope of DFT...

- Energetics, relative stability of different structures
Phase diagrams
 - Structural properties, geometry
 - Response to external perturbations
Elastic, Dielectrics, Piezoelectric constants
 - Vibrational properties
 - Chemical potential, Ionization energies, electron affinities, Fermi energy
 - Defect energetics and transport properties
- ... and many are NOT
- Electronic excitations (unless ΔE_G s)
 - Fermi surfaces and Band Structures
 - Defect induced electronic structure changes
 - electronic transport properties

DENSITY FUNCTIONAL THEORY

- Every observable quantity of a stationary quantum mechanical system is determined by the ground-state density alone.
- The ground-state density of the interacting system of interest can be calculated as ground-state density of an auxiliary non-interacting system in an effective potential

Electronic Problem:

$$H = T_e(\mathbf{r}) + V_e(\mathbf{r}) + V_{en}(\mathbf{r}_1, \mathbf{r}_2) + V_{nn}(\mathbf{R})$$

nitrogen atom:

7 electrons
21 coordinates

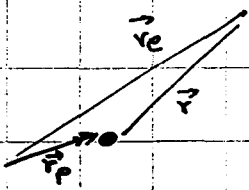
rough table of wave function:

10 entries per coordinate: 10^{21} entries

4 bytes per entry: 4×10^{21} bytes

100 Gbytes per HD: 4×10^{10} HDs

Hydrogen Atom: 1e 1p.



$$H = \frac{p_p^2}{2M_p} + \frac{p_e^2}{2m_e} - \frac{e^2}{|\vec{r}_e - \vec{r}_p|}$$

- Adiabatic Approx

$$H^{el}(r_p) = \frac{p_e^2}{2m_e} - \frac{e^2}{|\vec{r}_e - \vec{r}_p|}$$

$$E_{GS}^{el}(r_p) = \frac{m_e e^4}{2\hbar^2} = 1 \text{ Ry} = 13.6058 \text{ eV}$$

$$H = \frac{p_p^2}{2M_p} + E_{GS}^{el} \longrightarrow E_{GS} = E_{GS}^{el}$$

- Exact solution

$$\begin{cases} \vec{r}_e \\ \vec{r}_p \end{cases} \longrightarrow \begin{cases} \vec{r} = \vec{r}_e - \vec{r}_p \\ \vec{R} = \frac{m_e \vec{r}_e + m_p \vec{r}_p}{m_e + m_p} \end{cases}$$

$$\begin{aligned} \vec{p} &= m_e \vec{p}_e - m_p \vec{p}_p \\ \vec{P} &= \vec{p}_e + \vec{p}_p \end{aligned}$$

$$H = \frac{p^2}{2M} + \frac{p^2}{2\mu} - \frac{e^2}{r};$$

$$\begin{aligned} M &= m_e + m_p \\ \frac{1}{\mu} &= \frac{1}{m_e} + \frac{1}{m_p} \end{aligned}$$

$$E_{GS} = \frac{\mu e^4}{2\hbar^2} = 1 \text{ Ry}(H)$$

$$\Rightarrow \frac{E_{GS}(AA)}{E_{GS}} = \frac{m_e}{\mu} = 1 + \frac{m_e}{m_p} = 1 + 5 \times 10^{-4}$$

Adiabatic Approximation

2 different "phases": electrons and atoms (ions)

$$M_{\nu} \approx 2000 - 100000 m_e$$

$$Z_{\text{eff ion}} \approx 1$$

$$\Rightarrow \hbar\omega_{\text{ion}} \sim 10 \text{ meV} \quad \hbar\omega_{\text{el}} \sim 1 \text{ eV}$$

$$\hbar\omega_{\text{ion}} \ll \hbar\omega_{\text{el}}$$

$$\tau_{\text{ion}} \gg \tau_{\text{el}}$$

On the time scale electrons need to readjust themselves
ions ~~at~~ essentially don't move

$$\Psi(r, R) = \chi(R) \Phi(r; R)$$

neglecting $\nabla_R \Phi(r; R)$

$$\frac{[T_e + V_{ee} + V_{en} + V_{nn}] \Phi(r; R)}{\Phi(r; R)} + \frac{T_n \chi(R)}{\chi(R)} = E$$

$$\begin{array}{l} \text{QM!} \\ \text{QM or} \\ \text{EM} \end{array} \left\{ \begin{array}{l} [T_e + V_{ee} + V_{en} + V_{nn}] \Phi(r; R) = E_{\downarrow}(R) \Phi(r; R) \\ [T_n + E_{\downarrow}(R)] \chi(R) = E_{\downarrow \uparrow \downarrow} \chi(R) \end{array} \right.$$

\hookrightarrow Potential Energy Surface (PES)
usually the GS

next step: include electron-phonon interaction

electrons + ions

$$i\frac{\partial\Psi(\mathbf{r}, \mathbf{R})}{\partial t} = H(\mathbf{r}, \mathbf{p}, \mathbf{R}, \mathbf{P})\Psi(\mathbf{r}, \mathbf{R})$$

$$H(\mathbf{r}, \mathbf{p}, \mathbf{R}, \mathbf{P}) = T_I(\mathbf{P}) + T_e(\mathbf{p}) + \\ W_{II}(\mathbf{R}) + W_{ee}(\mathbf{r}) + \\ W_{eI}(\mathbf{r}, \mathbf{R})$$

$$\mathbf{r} = \vec{r}_1, \dots, \vec{r}_N, \quad \mathbf{R} = \vec{R}_1, \dots, \vec{R}_M, \\ 3(N + M) \text{ variables}$$

Exactly solvable: Hydrogen atom, harmonic oscillator.
Numerically solvable: single-particle problems.

Nevertheless

- GS geometry within 1-2 %
- elastic constants within 5-10 %
- lattice vibrations within a few %
- phase transitions under pressure correctly described
- and much more ...

Thanks to

- Adiabatic Approximation
- Density Functional Theory
- Powerful Computers and Efficient Algorithms

Hamiltonian for molecules and solids

$$H = \sum_{i=1}^N \frac{p_i^2}{2m} + \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \frac{e^2}{|r_i - r_j|} \\ - \sum_{i=1}^N \sum_{\nu=1}^n \frac{Z_\nu e^2}{|r_i - R_\nu|} \\ + \sum_{\nu=1}^n \frac{P_\nu^2}{2M_\nu} + \frac{1}{2} \sum_{\substack{\nu,\mu=1 \\ \nu \neq \mu}}^n \frac{Z_\nu Z_\mu e^2}{|R_\nu - R_\mu|}$$

$n = \#$ of atoms (2-100 for molecules, ∞ for solids)

$N = \#$ of electrons

$$H = T_e(p) + V_{ee}(r) + V_{en}(r, R) + T_n(P) + V_{nn}(R)$$

Schrodinger eq.

$$H(r, p, R, P) \psi_i(r, R) = E_i \psi_i(r, R)$$

all properties can be derived from it